(12) UK Patent Application (19) GB (11) 2 290 488 (13) A

(43) Date of A Publication 03.01.1996

(21) Application No 9512610.8

(22) Date of Filing 21.06.1995

(30) Priority Data
(31) 06142953 (32) 24.06.1994 (33) JP

(71) Applicant(s)
Toyota Jidosha Kabushiki Kaisha

(Incorporated in Japan)

1 Toyota-cho, Toyota-shi, Aichi-ken, Japan

(72) Inventor(s)
Hiroshi Hirayama
Toshihiro Takada

(74) Agent and/or Address for Service
Urquhart-Dykes & Lord
91 Wimpole Street, LONDON, W1M 8AH,
United Kingdom

(51) INT CL^6
F01N 3/28 , B01J 35/00 // (B01D 53/94 175:10 179:00 185:10)

(52) UK CL (Edition O)
B1W WAX W10B W10C W10D W10Y W9A W9X W9Y

(56) Documents Cited
EP 0441062 A1 US 5106588 A US 4448756 A

(58) Field of Search
UK CL (Edition N) B1F , B1W
INT CL^6 B01D 53/94 , B01J 35/00 , F01N 3/28

(54) **Exhaust emission control device for internal combustion engines**

(57) A catalyst for controlling exhaust emission and carried on catalyst carrier is provided in the exhaust gas passage of an internal combustion engine, wherein the catalyst is constituted with a first catalyst section which occupies the flow-in end portion of the catalyst and a second catalyst section which occupies the flow-out portion of the catalyst provided subsequent to the first catalyst section, said first catalyst section contains palladium, the second catalyst section contains platinum and rhodium, and at least the first catalyst section does not contain cerium. A downstream catalyst comprising a three-way catalyst containing cerium is provided additionally downstream of the catalyst for controlling exhaust emission. By structuring the catalyst for controlling exhaust emission as described above, the deterioration of platinum and palladium carried on the catalyst carrier is prevented and the efficiency of exhaust emission control is enhanced significantly.

GB 2 290 488 A

Fig.1

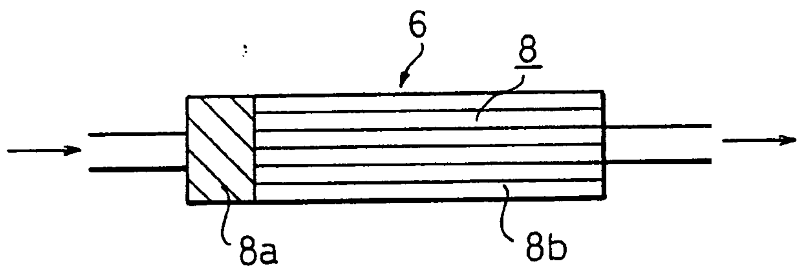


Fig.2

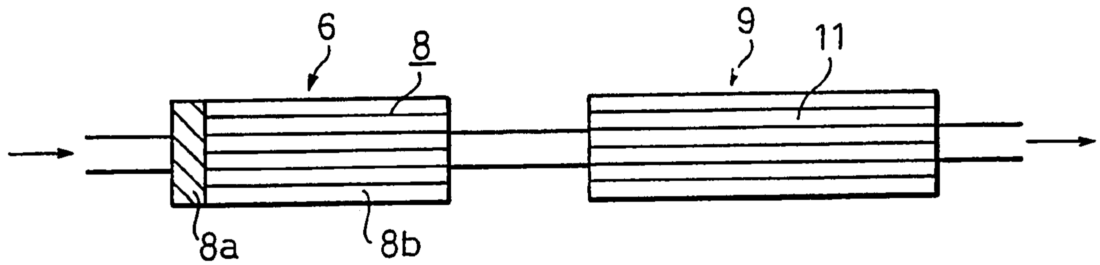


Fig.3

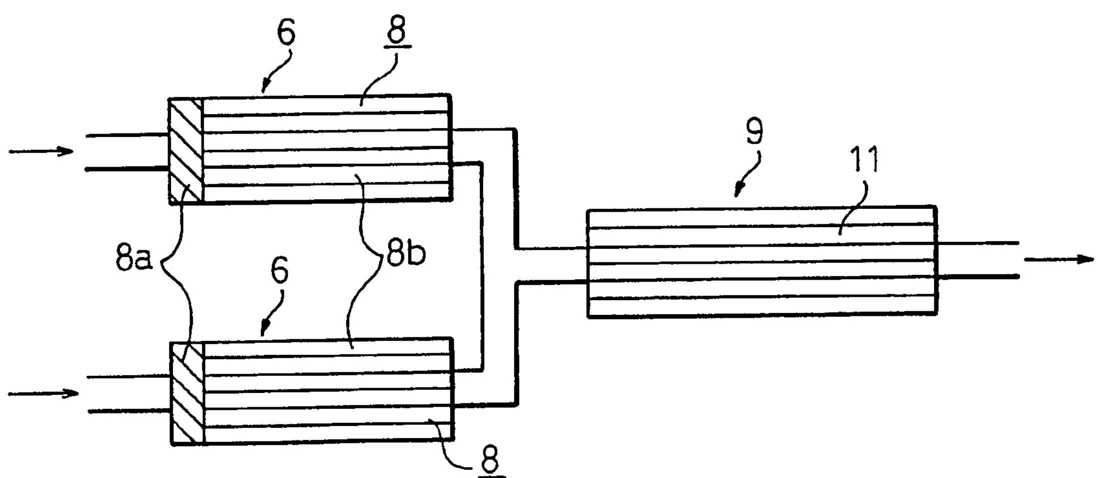
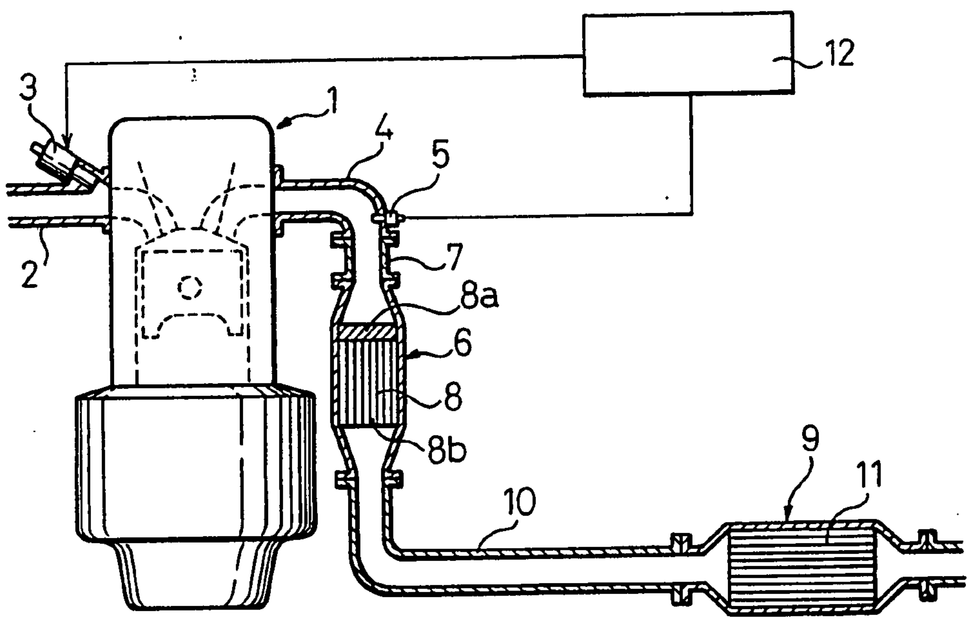
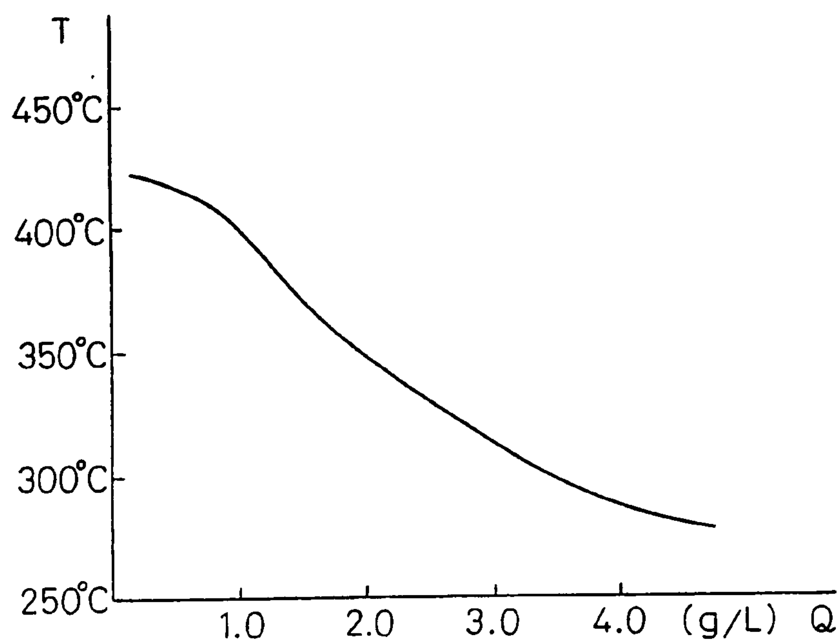


Fig.4



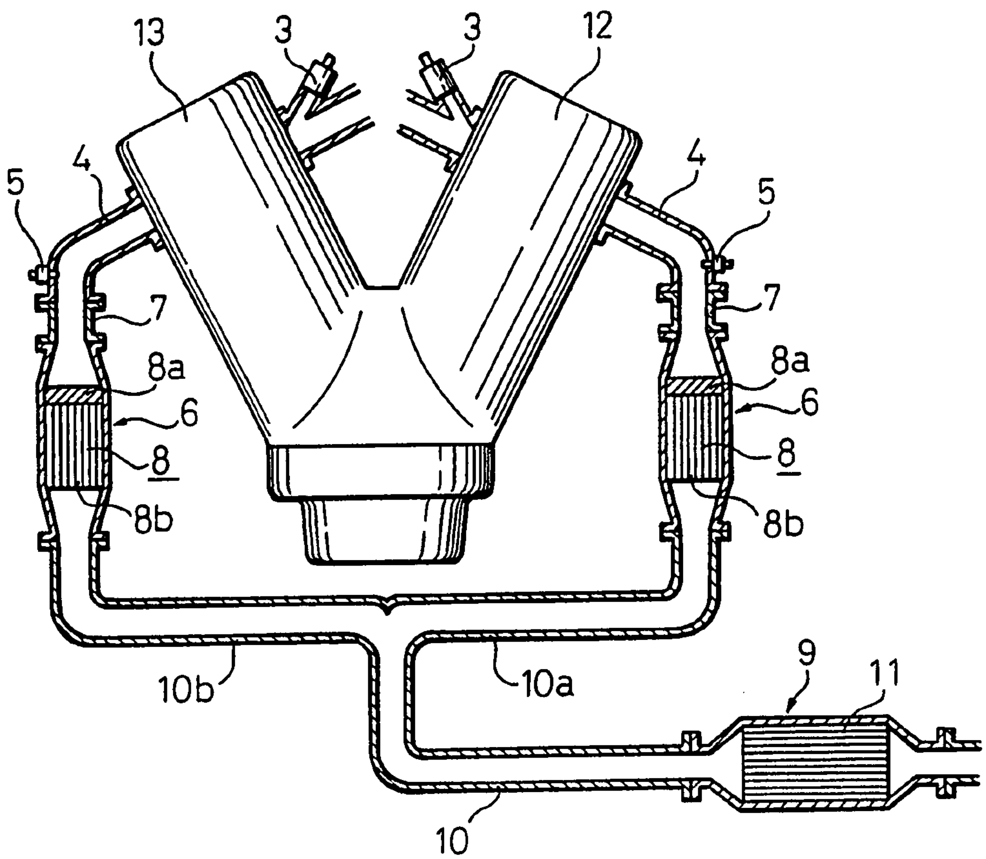
1
2
3
4
5
6
7
8
8a
8b
9
10
11
12

Fig.5



T
450°C
400°C
350°C
300°C
250°C
1.0
2.0
3.0
4.0
(g/L)
Q

Fig.6



EXHAUST EMISSION CONTROL DEVICE FOR INTERNAL COMBUSTION ENGINE

BACKGROUND OF THE INVENTION

1. Field of Utilization in Industry

The present invention relates to an exhaust emission control device for internal combustion engines, and more particularly relates to a device for controlling exhaust emission from internal combustion engines such as automobile engines. The internal combustion engines are also briefly referred herein to "engines".

2. Description of Related Art

Conventionally various catalysts or catalyst materials have been used for controlling exhaust emission from internal combustion engines. For example, a three way catalyst has been widely used for exhaust emission control devices because of the capability of removing three hazardous components contained in exhaust gas, carbon mono-oxide (CO), oxides of nitrogen (NO_x), and hydrocarbon (HC), simultaneously. However, the three way catalyst is generally poor in heat resistance, and is usually provided in a place where the heat is not severe, for example, in the exhaust passage far from an exhaust gas outlet of the engine, i.e., at the middle portion of the exhaust passage. By designing the exhaust system as described above, exhaust gas at a low temperature passes through the three way catalyst. This type of design has a disadvantage in that, by providing the three way catalyst at a place far from the outlet of the engine, the time from the ignition of the engine to the activation of the catalyst is prolonged, and during this time the device does not purify the exhaust gas. To solve the problem, a combination of the three way catalyst with another catalysts such as oxidation catalyst has been provided in an exhaust passage.

For example, an exhaust emission control device for internal combustion engines is disclosed in Japanese Unexamined Patent Publication (Kokai) No. 4-287820. In this exhaust emission control device, an oxidation catalyst containing palladium, which is excellent in heat resistance and oxidation capability, is provided in addition to a platinum catalyst near the exhaust gas outlet of the engine, and a three way catalyst is provided downstream of the oxidation catalyst in the exhaust gas passage. By employing the combination of an oxidation catalyst with a three way catalyst, high temperature exhaust gas generated in the internal combustion engine allows the oxidation catalyst to be activated immediately after ignition of the engine, the activation leads to immediate oxidation of HC to generate heat, and subsequently the heat due to the oxidation reaction favors the early activation of three way catalyst. In the case of this internal combustion engine, HC is removed by oxidation catalyst and CO and NO_x are removed by three way catalyst.

In Japanese Unexamined Patent Publication (Kokai) No. 62-136245, another catalyst device for controlling exhaust emission is disclosed. In this catalyst device, an upstream catalyst (first catalyst) is provided near the exhaust manifold, and a downstream catalyst (second catalyst) is provided in the exhaust gas passage in the downstream of the first catalyst. Based on the perception that it is difficult to sufficiently remove CO and NO_x using only one three-way catalyst, the catalyst device is constituted from a combination of first and second catalysts, wherein, in the first catalyst, platinum and rhodium, both having an oxidation-reduction function, namely, three way function, are provided on a catalyst carrier, in addition to palladium having an oxidation function.

In Japanese Unexamined Patent Publication

(Kokai) No. 4-118053, a catalyst for controlling exhaust emissions from engines is disclosed. In this catalyst system, four catalysts are provided, in series, in an exhaust passage of the engine the middle two catalysts being three-way catalysts containing platinum and rhodium, and a high concentration of palladium is provided at the flow-in end of each catalyst. In this catalyst system, an oxidation reaction of HC and CO in exhaust gas is proceeds at the flow-in end of each catalyst, due to the palladium, to generate heat of reaction, and the heat of the reaction allows the other catalysts to activate immediately.

Japanese Unexamined Patent Publication (Kokai) No. 62-68543 discloses a monolithic catalyst for controlling exhaust emissions comprising the first alumina layer containing palladium and neodymium and the second alumina layer containing at least rhodium out of platinum and rhodium and at least one component out of lanthanum and cerium. The monolithic catalyst is constituted of two catalyst groups and the problem of negative interaction between catalyst metals is solved by separating the catalyst metals into two groups, and thus the catalytic activity of each catalyst metal is kept high.

US Patent Specification No. 5,106,588 discloses a monolithic catalyst for controlling exhaust emissions. The monolithic catalyst features a structure having at least two catalyst blocks, that is, a catalyst block containing high concentration of palladium is provided upstream and a catalyst block containing platinum and rhodium is provided downstream. Especially when the catalyst is used for the exhaust emission system of an internal combustion engine which uses alcohols such as methanol, the catalyst remarkably reduces the aldehyde contained in the exhaust gas.

In US Patent Specification No. 4,448,756, a method for treating exhaust gas generated by an internal

combustion engine, in which exhaust gas is treated successively by passing it through a first catalyst containing finely divided palladium and then a second catalyst containing platinum and rhodium (three way catalyst), is disclosed. The thermal damage to the three way catalyst is prevented by this method because exhaust gas is treated with palladium prior to the treatment with the three way catalyst.

However, some problems remain unsolved in these conventional catalysts. For example, the above mentioned Japanese Unexamined Patent Publication (Kokai) No. 62-136245 discloses a catalyst system in which an oxidation catalyst containing platinum and rhodium, which exhibits a strong reducing capability especially to NO_x, is provided upstream of a three way catalyst in addition to palladium which accelerates oxidation because only one three way catalyst provided downstream is not enough to remove NO_x sufficiently, however, the catalytic deterioration of platinum cannot be avoided due to the homogeneous distribution of palladium, platinum, and rhodium in the catalyst.

The upstream catalyst is exposed to high temperature exhaust gas because the catalyst is provided near the outlet of an exhaust manifold. The air fuel ratio alternates between lean and rich because of three way catalyst, and the consequently exhaust gas which flows through the upstream catalyst can contain an excessive amount of oxygen. In the high temperature atmosphere containing excessive oxygen, Pt changes to PtO_2 (platinum oxide), and then the PtO_2 particles coagulate with each other to increase the grain size and large particles are formed. The surface area is decreased and the catalytic function is reduced due to the growth of Pt particles. The inclusion of platinum in an upstream catalyst results in a deterioration of the platinum catalytic capability and consequently the

oxidation reduction capability of the platinum and the rhodium is reduced.

An exhaust emission control device disclosed in Japanese Unexamined Patent Publication (Kokai) No. 4-287820 also involves the problem of platinum deterioration. In the case of this exhaust emission control device, an oxidation catalyst provided upstream of the device is exposed to a high temperature atmosphere, therefore, exhaust gas flowing into the oxidation catalyst can contain an excessive amount of oxygen, and, consequently, the platinum can be deteriorated.

In the case of the catalyst for controlling exhaust emission disclosed in Japanese Unexamined Patent Publication (Kokai) No. 4-118053, palladium is concentrated at the flow-in end portion of the catalyst and platinum is distributed throughout the catalyst. When exhaust gas generated by an engine flows into the catalyst, oxygen in the exhaust gas is consumed through oxidation with palladium and, consequently, the exhaust gas flowing through the downstream portion of the catalyst contains less oxygen than that flowing through the flow-in end portion. The oxygen concentration is not sufficient to cause the above mentioned oxidation reaction of platinum distributed in the downstream portion of the catalyst, thus the deterioration of platinum is prevented. However, the deterioration of platinum contained in the flow-in end portion of the catalyst can not be prevented because sufficient oxygen is present.

In addition to the above disadvantage, not only platinum but also palladium are deteriorated in the above mentioned engine. Palladium Pd changes to stable palladium oxide PdO in an atmosphere containing excessive oxygen and is reduced to unstable metallic palladium Pd in an atmosphere containing less oxygen, different from platinum. When the oxygen concentration in the exhaust

gas becomes excessive, palladium changes to palladium oxide on all such occasions and palladium will not grow to larger particle, however, when palladium is exposed continuously in an exhaust gas atmosphere containing less oxygen, metallic palladium coagulates to cause particle growth, consequently the palladium is deteriorated.

In the case of this engine, cerium is provided, in addition to platinum and rhodium, on the catalyst carrier in the flow-in end portion of the catalyst. Cerium has a so-called "oxygen storage function" that is, cerium absorbs oxygen from exhaust gas to remove NO_x when air fuel ratio is lean, and desorbs the oxygen to remove unburnt HC and CO when the air-fuel ratio is rich. Therefore, the existence of cerium in the catalyst causes a continuous deficiency of oxygen and the palladium particles grow larger to deteriorate the catalytic capability.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved exhaust emission control device for internal combustion engines having no disadvantages as mentioned above, that is, that the platinum and palladium used as catalytic metals in the device will not deteriorate.

It is a further object of the invention to provide an improved exhaust emission control device excellent in catalytic activity and exhaust emission control performance which can remove hazardous exhaust gas components of carbon monoxide (CO), oxides of nitrogen (NO_x), and hydrocarbon (HC) simultaneously.

Other objects of the invention will be easily understood by referring to the detailed description of the invention.

According to the present invention, an exhaust emission control device for internal combustion engines used for internal combustion engines so structured as to maintain the air fuel ratio approximately at the

theoretical value using an output signal from an air fuel ratio sensor provided in the exhaust gas passage, wherein a catalyst, for controlling exhaust emission and carried on catalyst carrier, is provided in the exhaust gas passage, which catalyst is constituted with two sections comprising the first catalyst section which occupies the exhaust gas flow-in portion of the catalyst and the second catalyst section which occupies the exhaust gas flow-out portion of the catalyst provided subsequent to the first catalyst section, the first catalyst section contains palladium and the second catalyst section contains platinum and rhodium, and at least the first catalyst section does not contain cerium, is provided. The catalyst for an exhaust emission control device constituted by the first and the second catalyst sections is referred as the first oxidation catalyst to differentiate the catalyst from three way catalyst which contains cerium as described in detail herein.

In the exhaust emission control device of the present invention, cerium is not contained in the first catalyst section and, also, may not be contained in the second catalyst section, that is, no inclusion of cerium in the first or the second catalyst sections is preferable for the oxidation catalyst.

In the first catalyst section of the first oxidation catalyst, it is preferable that 1.0g or more of palladium is carried on catalyst carrier per one liter of displacement of the engine.

For the exhaust emission control device of the present invention, it is preferable that a three way catalyst for controlling exhaust emission (referred as the second three way catalyst hereinafter) containing cerium carried on catalyst carrier is provided downstream of the first oxidation catalyst in addition to the first oxidation catalyst.

Though the second three way catalyst used in the exhaust emission control device of the present invention

can be variously combined with the first oxidation catalyst, it is preferable that both catalysts are provided apart each other in the exhaust gas passage.

Though the second three way catalyst may be composed of various catalytic metals, it is preferable that catalyst carrier carries platinum, rhodium, and cerium.

For the exhaust emission control device of the present invention, it is preferable that the first oxidation catalyst is provided near the outlet of exhaust manifold of the internal combustion engine and the second three way catalyst is provided under the floor of the body of an automobile equipped with the internal combustion engine. The air fuel ratio sensor is preferably provided upstream of the first oxidation catalyst in the exhaust gas passage from the internal combustion engine.

In the exhaust emission control device of the present invention, mainly hydrocarbon (HC) is oxidized, with aid of palladium carried on catalyst carrier, in the flow-in end portion of the first oxidation catalyst (first catalyst section). No inclusion of cerium on catalyst carrier of the first catalyst section results in alternate excessive oxygen concentration in exhaust gas flowing in the catalyst section, consequently the palladium will not deteriorate. There is neither platinum nor rhodium on the catalyst carrier in the first catalyst section, therefore there is no problem of platinum deterioration regardless of alternate excessive oxygen concentration in exhaust gas flowing in the first catalyst section. Excessive oxygen in the exhaust gas is consumed through an oxidation reaction with aid of palladium and, consequently, only a reduced amount of oxygen is contained in the exhaust gas when the exhaust gas enters the residual portion of the catalyst (second catalyst section) downstream of the first catalyst section and the reduced oxygen concentration does not lead to deterioration of the platinum contained in this

catalyst section.

For the exhaust emission control device of the present invention, by having cerium in the second three way catalyst downstream of the first oxidation catalyst, the oxidation reduction capability of the device of the invention is additionally enhanced.

Therefore, according to the present invention, unburnt HC, CO, and NO_x in exhaust gas can be removed while the deterioration of the platinum and the palladium carried on the catalyst carrier is prevented.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram illustrating a preferred embodiment of the exhaust emission control device for internal combustion engines in accordance with the present invention.

Fig. 2 is a schematic diagram illustrating another preferred embodiment of the exhaust emission control device in accordance with the invention.

Fig. 3 is a schematic diagram illustrating a further preferred embodiment of the exhaust emission control device in accordance with the invention.

Fig. 4 is a general view illustrating an internal combustion engine equipped with the exhaust emission control device in accordance with the invention.

Fig. 5 is a graph describing the relation between the amount of palladium content Q in catalyst carrier and the temperature T of the catalyst when the removal of unburnt hydrocarbon (HC) reaches 50%.

Fig. 6 is a general view for illustrating a different embodiment of an internal combustion engine equipped with the exhaust emission control device in accordance with the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The preferred embodiments of the present invention will be described, in detail, by referring to attached drawings. It should be understood that the present

invention is by no means limited to the embodiments described hereinafter.

Fig. 1 is an illustration of a preferred embodiment of the exhaust emission control device for internal combustion engines in accordance with the present invention. The exhaust emission control device is provided preferably in a form of catalytic converter 6, and provided in exhaust gas passàges extending from exhaust manifolds of an internal combustion engine as illustrated in the figure as is usual in the art (arrows in the figure indicate the flow direction of exhaust gas). The catalytic converter 6 illustrated in the figure may be provided at or near the exhaust manifold of the internal combustion engine if required. The catalyst 8 for controlling exhaust emission of the catalytic converter 6 comprises catalyst components of noble metal particles carried on a catalyst carrier, and preferably is a monolithic catalyst (or a honeycomb catalyst). Conventional pellet catalysts may be used if the catalysis is comparable. The monolithic structure of the exhaust emission control device in accordance with the present invention is formed according to techniques generally employed in the art. For example, a monolithic carrier having many through holes in the flow direction of exhaust gas is made using a ceramic material such as a cordierite ceramic excellent in heat resistance and having reduced thermal expansion or metallic materials such as stainless steel, and catalyst coating is applied on the surface of the carrier. The catalyst coating layer is also referred to as wash coat, and the coating layer has usually a layer thickness of 0.01 to 0.5 mm, preferably about 0.05 mm, a specific surface of about 50 to 200 m^2/g and fine pores with a diameter of about 10 nm or less. The catalyst layer is preferably formed, for example, by dispersing fine particles of a noble metal catalyst component homogeneously on the surface of a

porous material such as activated alumina (aluminum oxide). Though the size of the noble metal fine particles to be dispersed on the catalyst layer is selected variously in a wide range depending on various factors such as desired catalysis and the structure of the catalyst carrier, the size ranges from about 0.1 to 10 nm in general, and is preferably several nm.

The catalyst 8 for controlling exhaust emissions of the invention is constituted with a first catalyst section 8a which occupies the flow-in portion of the catalyst and a second catalyst section 8b which occupies the flow-out portion of the catalyst subsequent to the first catalyst section 8a as illustrated in the figure. In the catalyst 8 of the present invention, one catalyst zone is divided to front and rear portions in the flow direction of exhaust gas to separate the catalytic function, whereby the object of the invention is accomplished. Especially, the catalyst 8 of the invention features a first catalyst section 8a containing palladium and no cerium and a second catalyst section 8b containing platinum and rhodium. Cerium may be contained in the second catalyst section 8b if required. For the catalyst 8 of the invention, fine particles of noble metals other than these described above may be contained additionally as usual in the art if a desirable additional effect can be expected from the addition and without an adverse effect on the catalysis.

For the catalyst 8 of the invention, the existence of the first catalyst section 8a and inclusion of palladium in the section are very important. The proportion of the first catalyst section 8a in the first oxidation catalyst 8 may be varied depending on the structure of the catalyst 8 and other various factors, but in general a small portion of the whole catalyst zone may be enough. The preferable proportion is about 10 to 35% of the whole catalyst zone at the flow-in side. The amount of palladium to be carried on catalyst carrier of

the first catalyst section 8a is preferably 1.0g or more per one liter of displacement for one cylinder engine to exhibit the maximum effect of the palladium addition.

Fig. 2 illustrates another preferred embodiment of the exhaust emission control device for internal combustion engines in accordance with the present invention. The exhaust emission control device of the invention is preferably constituted by combining the catalytic converter 6 (the first oxidation catalyst 8) described hereinbefore referring to Fig. 1 with a catalytic converter 9 comprising three way catalyst for controlling exhaust emission 11 (the second three way catalyst) containing cerium carried on catalyst carrier, which catalytic converter 9 is provided downstream. The second three way catalyst 11 is structured in the same manner as described above in the description of the first oxidation catalyst 8, therefore, the second three way catalyst is preferably a monolithicic type. Noble metals to be dispersed on the catalyst layer are cerium as essential component and preferably platinum and rhodium. The catalyst 11 may contain fine particles of other noble metals as in the catalyst 8.

In the practice of the invention, the first upstream catalyst 8 and the second downstream catalyst 11 are preferably connected in series but separated by the exhaust passage as shown in Fig. 2. However, if the intermediate exhaust passage can be eliminated because of a favorable structure of the internal combustion engine, both the first oxidation catalyst and the second three way catalyst may be contained together in single catalytic converter. In the example shown in Fig. 2, a system having one manifold from an internal combustion engine (not shown) and accordingly one exhaust passage is illustrated, however, in the case that the system has two internal combustion engines and one exhaust emission control device, two exhaust passages may be combined just before the first oxidation catalyst 8. Alternatively,

preferably, a first oxidation catalyst 8 may be provided for each internal combustion engine, but only one second three way catalyst 11 may be used commonly subsequent to the first oxidation catalysts 8 as illustrated in Fig. 3.

The exhaust emission control device in accordance with the present invention is manufactured according to conventional techniques used in the art generally. Therefore, a detailed description of the manufacture of catalyst carrier, deposition of the catalyst component, and fabrication of catalytic converter are omitted in this patent specification. Details are described in, for example, Japanese Unexamined Patent Publication (Kokai) Nos. 62-68543 and 62-136245 described hereinbefore for reference.

Referring to Fig. 4, 1 is the body of a internal combustion engine, 2 is an inlet manifold branch pipe, 3 is a fuel injection valve mounted on each inlet manifold branch pipe 2, 4 is an exhaust manifold, 5 is an air fuel ratio sensor provided in a joining zone of the exhaust manifold 4, 6 is an upstream catalytic converter connected to the outlet of the exhaust manifold 4 spaced with a short exhaust pipe 7 and containing an upstream catalyst 8, and 9 is a downstream catalytic converter connected to the outlet of the upstream catalytic converter 6 but separated by an exhaust pipe 10 and containing a downstream catalyst 11. The upstream catalytic converter 6 is provided near the outlet of the exhaust manifold 4 to receive high temperature exhaust gas and, on the other hand, the downstream catalytic converter 9 is provided under the floor of the automobile body to receive low temperature exhaust gas.

The air fuel ratio sensor generates an output signal for indicating a lean or rich air-fuel ratio, and the output signal is input to a controller 12. The controller 12 controls the fuel injection from the fuel injection valve 3 based on the output signal. When the air fuel ratio sensor generates an output signal

indicating lean in the air fuel ratio, the fuel injection is increased slowly, and when the air fuel ratio sensor generates output signal indication rich in air fuel ratio, the fuel injection is decreased slowly. The air fuel ratio changes from lean to rich and from rich to lean alternately and repeatedly across the theoretical air fuel ratio, and consequently the air fuel ratio is maintained near the theoretical air fuel ratio.

In the embodiment shown in Fig. 4, both the upstream catalyst 8 and downstream catalyst 11 are formed of a monolithic catalyst, and the upstream catalyst 8 has smaller capacity than the downstream catalyst 11. The upstream catalyst 8 comprises the flow-in end section 8a and a remaining catalyst section 8b provided downstream of the flow-in end section 8a, wherein both sections contain different catalysts. The catalyst carrier at the flow-in end section 8a contains an oxidation catalyst and the catalyst carrier of the residual catalyst section 8b contains an oxidation reduction catalyst, namely a three-way catalyst.

In the embodiment shown in Fig. 4, palladium Pd is dispersed uniformly in the radial direction and the axis direction is carried on the catalyst carrier at the flow-in end section 8a, and platinum and rhodium Rh, dispersed uniformly in the radial direction and the axis direction is carried on the catalyst carrier of the residual catalyst section 8b. Neither platinum Pt nor rhodium Rh are carried on catalyst carrier at the flow-in end section 8a and no palladium Pd is carried on the catalyst carrier at the remaining catalyst section. In the embodiment shown in Fig. 4, cerium Ce is not carried on catalyst carrier of the flow-in end section 8a or on catalyst carrier of the remaining catalyst section 8b. In the embodiment shown in the figure, cerium Ce may be carried on only the catalyst carrier at the residual catalyst section, but from the view point of easy manufacturing, it is preferable that no cerium is carried

on any of the catalyst carrier in the upstream catalyst 8.

On the other hand, the downstream catalyst 11 comprises a three way catalyst. On the catalyst carrier of the downstream catalyst 11, platinum Pt and rhodium Rh, which are oxidation reduction catalysts and have strong reduction capacity for NO_x, are carried and, further more, cerium Ce is carried on the downstream catalyst 11 to enhance the oxidation reduction capability.

During the operation of the engine, the air-fuel ratio is switched alternately between lean and rich based on output signal generated from the air fuel ratio sensor 5 and consequently the air fuel ratio is maintained near the theoretical air fuel ratio. The lange amount of unburnt HC and the small amount of unburnt CO contained in exhaust gas is oxidized with the aid of palladium Pd carried on catalyst carrier of the flow-in end section 8a of the upstream catalyst 8. As described hereinbefore, cerium Ce is carried on the catalyst carrier at the flow-in end section 8a, therefore, the oxygen concentration of the exhaust gas flowing into the flow-in end section 8a can be excessive. Consequently, palladium Pd is changed to stable palladium oxide PdO but the palladium Pd is not maintained for long in the metallic state and this prevents palladium Pd particles from growing and the palladium will not deteriorate.

As described hereinbefore, platinum Pt and rhodium Rh are not carried on the catalyst carrier at the flow-in end section 8a. Therefore, there is no problem of platinum Pt deterioration at the flow-in end section 8a.

Exhaust gas which has passed through the flow-in end section 8a enters the residual catalyst section 8b, where oxidation of CO and reduction of NO_x proceed. The temperature of exhaust gas which is flowing into the residual catalyst section 8b is high, therefore, if the

oxygen content in the exhaust gas is high, platinum Pt changes to platinum oxide PtO to result in particle growth. However, oxygen in the exhaust gas is consumed by an oxidation reaction with aid of palladium Pd in the flow-in end section 8a, and only a reduced amount of oxygen in the exhaust gas flows into the residual section 8b and, consequently, platinum Pt does not change to platinum oxide PtO_2 and there is no problem of particle growth of platinum Pt. Therefore, the platinum Pt does not deteriorate.

Next, the exhaust gas flows into the downstream catalyst 11, is oxidized and the NO_x is reduced. When the exhaust gas enters into the downstream catalyst 11, the temperature of the exhaust gas is lowered, and oxygen concentration in the exhaust gas which enters into the downstream catalyst 11 is lowered. Therefore, there is no problem of particle growth due to the change from platinum Pt to platinum oxide PtO_2.

On the other hand, hot exhaust gas flows into the upstream catalyst 8 immediately after the ignition of the engine because the upstream catalyst is provided near the outlet of the exhaust manifold 4 and the hot exhaust gas helps activate the upstream catalyst. The activated upstream catalyst 8 initiates an oxidation reaction in the flow-in end section 8a, and the heat of reaction due to the oxidation reaction immediately activates the catalyst in the residual catalyst section 8b and the downstream catalyst 11.

Fig. 5 describes the relation between the palladium Pd content Q and the temperature T of the upstream catalyst 8 when the removal of unburnt HC reaches 50% with the aid of palladium Pd carried on the catalyst carrier at the flow-in end section 8a of the upstream catalyst 8. The palladium Pd content Q is represented by amount in gram per one liter of displacement (g/L) for one cylinder engine. The lower temperature T of the

upstream catalyst 8 in Fig. 5 means the prompt removal of unburnt HC after the ignition of the engine, therefore, a lower temperature of the upstream catalyst 8 is more preferable. In the embodiment of the present invention, the palladium Pd content is 1.0g or more per one liter of displacement for one cylinder engine.

In the embodiment shown in Fig. 4, the platinum Pt carried on catalyst carrier of the upstream catalyst 8 is 1.5g per one liter of catalyst, and rhodium Rh content carried on catalyst carrier of the upstream catalyst 8 is about 0.3g per one liter of catalyst. The platinum Pt content and rhodium Rh content carried on catalyst carrier of the downstream catalyst 11 are about 1.0g and 0.2g per one liter of catalyst, and the cerium Ce content carried on catalyst carrier of the downstream catalyst 11 is 0.3 to 0.45 moles per one liter of catalyst.

Fig. 6 shows the application of the exhaust emission control device of the present invention to a V-engine. In this figure, the constitutional elements are assigned the same symbols as assigned in Fig. 4 to the corresponding constitutional elements. In the embodiment shown in Fig. 6, exhaust manifolds 4 are connected respectively to each bank 12, 13 of the engine body, and each manifold 4 is connected separately to upstream catalytic converters 6 with intervening exhaust pipes 7. In each upstream converter 6, an upstream catalyst 8 similar to the upstream catalyst 8 shown in Fig. 4 is provided respectively. Each upstream catalytic converter 6 is connected to a joined exhaust pipe 10 with intervening exhaust pipes 10a and 10b, the exhaust pipe 10 is connected to a downstream catalytic converter 9. In the downstream converter 9, a downstream catalyst 11 similar to the downstream catalyst 11 shown Fig. 4 is provided.

CLAIMS

1. An exhaust emission control device used for internal combustion engines which are so structured as to maintain the air fuel ratio at approximately the theoretical air fuel ratio based on output signal generated from an air fuel ratio sensor provided in the exhaust gas passage, provided with a catalyst, for controlling exhaust emission, carried on a catalyst carrier in said exhaust passage wherein said catalyst is constituted with a first catalyst section which occupies the flow-in end portion of said catalyst and a second catalyst section which occupies the flow-out side portion of said catalyst provided subsequent to said first catalyst section, palladium is contained in said first catalyst section and platinum and rhodium are contained in said second catalyst section, and cerium is not contained at least in said first catalyst section.

2. An exhaust emission control device as claimed in claim 1, wherein cerium is not contained in said catalyst, for controlling exhaust emission, in a full area of said first and second catalyst sections.

3. An exhaust emission control device as claimed in claim 1 or claim 2, wherein said catalyst for controlling exhaust emissions is provided near an exhaust manifold of said internal combustion engine.

4. An exhaust emission control device as claimed in any one of claims 1 to 3, wherein a three way catalyst for controlling exhaust emissions containing cerium carried on a catalyst carrier is provided downstream of said catalyst for controlling exhaust emission in addition to said catalyst for controlling exhaust emission.

5. An exhaust emission control device, as claimed in claim 4, wherein said catalyst for controlling exhaust emissions is connected to said catalyst for controlling exhaust emissions with an intervening exhaust gas passage.

6. An exhaust emission control device as claimed in claim 4 or claim 5, wherein said three-way catalyst for controlling exhaust emissions contains platinum, rhodium, and cerium carried on catalyst carrier.

7. An exhaust emission control device as claimed in any one of claims 4 to 6, wherein said three-way catalyst for controlling exhaust emissions is provided under the floor of a body of an automobile equipped with said internal combustion engine.

8. An exhaust emission control device as claimed in any one of claims 1 to 7, wherein the amount of palladium carried on the catalyst carrier in said first catalyst section is 1.0g or more per one liter of displacement for one cylinder engine.

9. An exhaust emission control device as claimed in any one of claims 1 to 8, wherein said air fuel ratio sensor is provided upstream of said catalyst for controlling exhaust emission in said exhaust gas passage.

10. An exhaust emission control device substantially as hereinbefore described with reference to any one of the Figures of the accompanying drawings.

Patents Act 1977 **Examiner's report to the Comptroller under Section 17** **(The Search report)** 20	Application number GB 9512610.8
Relevant Technical Fields (i) UK Cl (Ed.N) B1W, B1F (ii) Int Cl (Ed.6) B01D (53/94), B01J (35/00), F01N (3/28)	Search Examiner J H WARREN Date of completion of Search 13 SEPTEMBER 1995
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii)	Documents considered relevant following a search in respect of Claims :- 1-10

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	EP 0441062 A1	(NIPPON SHOKUBAI) Examples 2, 4 and 6; Table 1	1-3
X	US 5106588	(SIMS) column 4 lines 5 to 17	1-3
X	US 4448756	(HAMMERLE) column 3 line 46 to column 4 line 55	1-3

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).